Chem 4A, Fall 2006
Midterm exam 3, November 17, 2006
Prof. Head-Gordon; Prof. Moretto

Name: COMFORT KEY **TA:** ____________

Grade:

1. (7 points) ________
2. (1 point) ________
3. (4 points) ________
4. (4 points) ________
5. (~~[illegible]~~ points) 4 pts ________
6. (3 points) ________
7. (3 points) ________

Total: ________

Close book exam. There are 6 pages. Calculators are OK. Use back side of pages for scribble paper.

Some possibly useful facts and figures:

$R = 8.3145\ J\ mol^{-1}\ K^{-1}$

$k_B = 1.38066 \times 10^{-23}\ JK^{-1}$

molar volume at STP= 22.4 L

$N_0 = 6.0221 \times 10^{-23}\ mol^{-1}$

For 1 mole of ideal gas :

$E = 3/2\ RT$; $C_v = 3/2\ R$

$S = 3/2\ R\ln T + R\ln V$

Substance	ΔH_f^0 ($kJmol^{-1}$)	S° ($Jmol^{-1}K^{-1}$)	ΔG_f^0 ($kJmol^{-1}$)
$CH_{4(g)}$	-75	187	-51
$O_{2(g)}$	0	205	0
$H_2O(l)$	-286	70	-237
$H_2O(g)$	-242	189	-228
$CO_{2(g)}$	-395	214	-229
$CaCO_{3\,(s)}$	-1207	93	-1129
$CaO_{(s)}$	-635	40	-604

1. (7 points) Given the unbalanced reaction :

$$CH_4 + O_2 \leftrightarrow CO_2 + H_2O_{(l)}$$

a) (1point) balance the equation

$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

↑ ↑

b) Start with 1.0 moles of CH_4 and enough O_2 to burn it completely. Calculate:

- (2points) ΔH^0 ; ΔG^0

$\Delta H° = [-395 \frac{kJ}{mol} + 2(-286)] - [-75 + 2(0)] = \boxed{-892\ kJ/mol}$

$\Delta G° = [-229 \frac{kJ}{mol} + 2(-237)] - [-51 + 2(0)] = \boxed{-652\ kJ}$

- (2points) the initial and final volume at 1 Atm and 25°C (neglect the volume of liquids)

volume of 1 mol ideal gas @ STP (1 atm, 0°C) = 22.4 L (siska p. 29)

volume, initial: $(3\ mol)(22.4 \frac{L}{mol})(\frac{298\ K}{273\ K}) = \boxed{73.4\ L}$

volume, final: 1 mol → $\frac{1}{3} V_i = \boxed{24.5\ L}$

- (2points) the final temperature if you keep the initial volume fixed and the container isolated (Assume only translational degrees of freedom) . Should you take into account water molecules?

recalc. $\Delta H°$ for $H_2O(g)$: $[-395 \frac{kJ}{mol} + 2(-242)] - [-75 + 2(0)] = \boxed{-804\ kJ}$

$C_V = \frac{3}{2} nR = \frac{3}{2}$ (3 mol gas now!!) $(R) = \frac{9}{2} R = 37.4 \frac{J}{mol \cdot K}$

$E = -\Delta H° = +804\ kJ = \frac{3}{2} nR\Delta T = \frac{9}{2} R\Delta T = 37.4 \frac{J}{mol \cdot K} (\Delta T)$

$\Delta T = 21,489\ K$; $\boxed{T_{final} = 298\ K + \Delta T = 21,787\ K}$

2) (1point) A heat pump is used to keep a house at 25^{0}C. The outside temperature is 0^{0}C. Calculate the efficiency of an ideal heat pump. (Hint: it has better be >1!)

$$\varepsilon = \text{(heat out)} / \text{(electrical energy in)}$$

$$\varepsilon\text{, efficiency of heat pump} = \frac{T_1}{T_1 - T_2} = \frac{298}{298-273} = \boxed{11.92 \text{ or } 1192\%}$$

T_1 = larger temp = 298 K

T_2 = smaller temp = 273 K

3) (4 points) One mole of ideal gas at temperature T and volume V is expanded isothermally and reversibly to volume 2V.

- (2 points) Calculate **ΔS**

$$\Delta S = nR\ln\frac{V_2}{V_1} = (1\text{ mol})(R)\ln\left(\frac{2V_1}{V_1}\right)$$

$$\boxed{\Delta S = nR\ln 2 = R\ln 2 = 5.76 \text{ J/mol}\cdot\text{K}}$$

- (2 points) The same initial gas is adiabatically expanded with no external work to the same volume 2V.
  Calculate **ΔT and ΔS.**

"adiabatic" : $q = 0$

$\Delta E = q + w = 0 + 0 = 0$

$\Delta E = \frac{3}{2} nR\Delta T \rightarrow \boxed{\Delta T = 0}$

$\boxed{\Delta S = R\ln 2 = 5.76 \text{ J/mol}\cdot\text{K b/c state function}}$

↳ same as above value for ΔS

4) (4points) You toss 10 quarters of which n turn out heads. Each head will cost you the quarter . (cost is like energy)

- (2poinst) Write down the entropy S as a function of the total cost (energy). No calculations are needed

$$S = k\ln\Omega, \quad \Omega = \frac{N!}{n!\,(N-n)!}$$

$N = 10$
$n = "n"$

$$\rightarrow S = k\ln\frac{N!}{n!\,(N-n)!} = k\ln\frac{10!}{n!\,(10-n)!}$$

$$E = 0.25n \rightarrow n = E/0.25$$

$$\boxed{S = k\ln\frac{10!}{(E/0.25)!\,(10-E/0.25)!}}$$

- (2points) Can you figure out for which n is S maximum? (you can get the answer just by inspecting the formula)

$$S = k\ln\left[\frac{N!}{n!(N-n)!}\right]$$

note: This value must be + b/c you can't take the ln of a - value. Also $\ln(0) \rightarrow -\infty$, so this value must be ≥ 1; and note that $\ln(1) = 0$

$[\ ] = 1$ if $n = 0, 10$:

$$n = 0 \rightarrow \frac{10!}{0!\,(10-0)!} = \frac{10!}{10!} = 1$$

$$n = 10 \rightarrow \frac{10!}{10!\,(10-10)!} = \frac{10!}{10!} = 1$$

$\therefore$ minima occur @ $n = 0, 10$; if S is symmetric, then

maximum occurs @ n = 5

5) (4points) Consider the reaction

balanced!

↓

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2\,(g)}$$

- (2points) Calculate ΔH^0 ; ΔS^0 and ΔG^0. Is the reaction spontaneous at standard conditions?

$\Delta H^\circ = [-635 \frac{kJ}{mol} + -395] - [-1207] = \boxed{177\ kJ}$

$\Delta S^\circ = [40 \frac{J}{mol \cdot K} + 214] - [93] = \boxed{161\ J/K}$

$\Delta G^\circ = [-604 \frac{kJ}{mol} + -229] - [-1129] = \boxed{+296\ kJ}$

reaction is NOT spontaneous @ STP b/c $\Delta G^\circ = \oplus$

- (2points) Assuming ΔH^0 and ΔS^0 to be temperature independent, estimate at what temperature $\Delta G=0$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$0 = 177\ kJ - T(.161\ kJ/K)$

$\boxed{T = 1099\ K = 826\ ^\circ C}$

"10^{-10}" = 1×10^{-10}

6) (3points) The solubility product of AgCl is $K_{sp}=10^{-10}$. Calculate :

- (1point) the solubility of AgCl in pure water

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-] = 1 \times 10^{-10}$$
$$= [s][s] = 1 \times 10^{-10} = s^2$$

$$\boxed{s = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-10}} = 1.0 \times 10^{-5}\ M}$$

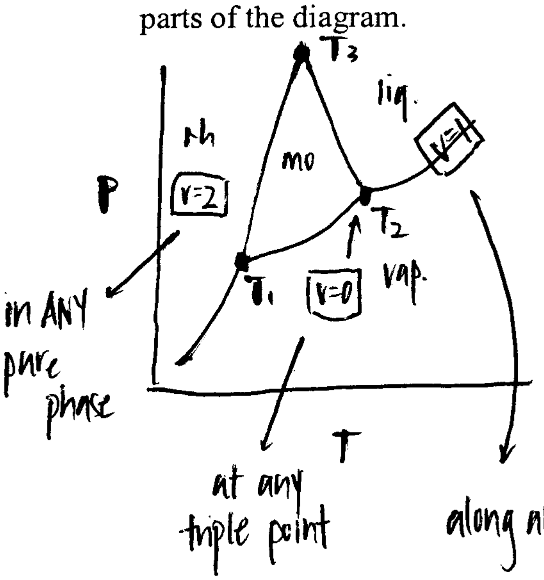
- (2points) the solubility of AgCl in a 1.0M NaCl.

$$NaCl \rightarrow Na^+ + Cl^- \quad (1.0\ M\ NaCl \rightarrow 1\ M\ Na^+ + 1\ M\ Cl^-)$$

$$K_{sp} = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$$
$$= [s][1.0\ M] = 1 \times 10^{-10}$$

$$\boxed{s = 1 \times 10^{-10}\ M}$$

7) (3 points) Sulphur has four phases : rhombic, monoclinic, liquid, gas. By means of Gibbs' rule calculate the maximum number of phases that can coexist. In a P,T phase diagram identify the triple points, the coexistence lines, and the variance in the relevant parts of the diagram.



Gibbs Phase Rule: $V = n - f + 2$

$0 = 1 - f + 2$

$\boxed{f = 3 = \text{max \# phases that coexist}}$

triple point(s): T1 : rh, mo, vapour
T2 : mon, liquid, vapour
T3 : rh, mo, liquid